A Comparison of Computerized Chemical Models for Equilibrium Calculations in Aqueous Systems[1]

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The interpretation of chemical processes in aqueous systems requires the use of modern electronic computers, particularly in the calculation of multicomponent, multiphase equilibria. Commonly, the first concern of solution chemists and aqueous geochemists is to calculate the distribution and activities of species on the assumption that equilibrium exists throughout the aqueous phase. Species distribution can then be used in several areas of analytical and applied chemistry, e.g. to examine the availability of free and reactive ions, to test solubility hypotheses, and to determine the potential bioavailability of nutrients or toxic substances. Species distribution also forms the basis for more complex computations involving solutions which change composition by reaction with other solutions and with gases and solids. Equilibrium calculations of this type are particularly helpful in solving interpretive problems encountered in such fields as chemical and environmental engineering, geochemistry, biochemistry and aquatic ecology.

This symposium demonstrates quite clearly that we depend heavily on chemical models, especially computerized models, to interpret aqueous chemical processes. Several computer programs which solve problems of simultaneous chemical equilibria are being used by a rapidly increasing number of investigators and it is necessary to review the inherent assumptions and limitations of these aqueous models. There is a temptation to use these models as ready-made interpretations

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of reality without a clear understanding of their weaknesses. These programs and models are usually developed for specific purposes and taken together they represent a wide range of capabilities and features. This paper reviews the state-of-the-art of equilibrium computations by providing a compilation and description of aqueous models in current use and by examining their consistency through a comparison of species distributions and saturation indices for two hypothetical test cases: a river water sample and a seawater sample. This review will also serve to complement the review on machine computation efficiency by Leggett (1) and the review by Perrin (2) on the applications of digital computers to analytical chemistry.

The Chemical Equilibrium Problem and Its Thermodynamic Basis

An "aqueous chemical model" needs to be defined separately from the computer program which executes calculations based on the model. Such a model can be defined as a theoretical construction which allows us to predict the thermodynamic properties of electrolyte solutions. There are several ways of constructing an aqueous model, e.g. from the Bjerrum ion association theory (3), or the Fuoss ion association theory (4,5) or the Reilly, Wood and Robinson mixed electrolyte theory (6). The choice of model must be made on the basis of the problem to be solved and each model carries with it its own set of assumptions and restrictions. Nearly all computerized models are based on the ion association theory and within this framework the species distribution problem can be formulated in two distinct but thermodynamically related ways: the equilibrium constant approach and the Gibbs free energy approach. Both approaches are subject to the conditions of 1) mass balance and of 2) chemical equilibrium. The mass balance condition requires that the computed sum of the free and derived (complexes) species be equal to the given total concentration. Chemical equilibrium requires that the most stable arrangement for a given system be found, as defined by the equilibrium constants for all mass action expressions of the system, or through the use of Gibbs free energies for all of the components and derived species. In the equilibrium constant approach the mass action expressions are substituted into the mass balance conditions resulting in a set of nonlinear equations which must be solved simultaneously. The Gibbs free energy approach is simply a transformation of variables through the thermodynamic relation:

$$\Delta G_r = \Delta G_r^\circ + RT\ln K = 0$$

which allows a different numerical approach. The total Gibbs

free energy function is then minimized for a given set of species and their mole numbers subject to the mass balance requirement. In the former approach equilibrium constants are needed for the data base whereas in the latter approach free energy values are needed. This difference in the data base can often be an important limitation. At the present time there are more reliable and available equilibrium constants than free energy values.

By either thermodynamic approach the problem can be stated numerically as one of finding a solution to a set of nonlinear equations. It is usually not feasible to simultaneously solve these equations in exact form for a multicomponent, multiphase system and therefore an iteration procedure must be utilized. The standard method of solving the problem by the equilibrium constant approach is to use linearized matrix inversion. Convergence assumes, of course, that the solution not only exists but that it is unique. If a system can have several thermodynamically metastable states (local minima in the Gibbs function) then several nonunique solutions are possible. Recent papers by Othmer (7) and Caram and Scriven (8) have pointed out that uniqueness is characteristic of ideal systems whereas for non-ideal systems a solution may occur at the global minimum (most stable equilibrium point) but it also may occur at a nonunique local minimum. For applications in aquatic chemistry the problem of nonuniqueness is particularly important in the interpretation of solid precipitation and dissolution processes.

The choice of the thermodynamic approach dictates the general category of numerical techniques to be used. Optimization techniques such as pattern search, linear programming, steepest descent and gradient methods are all appropriate to the Gibbs function approach whereas Newton-Raphson, successive approximations and nested iterations are best suited to the equilibrium constant approach. These techniques and several other mathematical methods have been documented along with the thermodynamic formalism in the excellent reviews by Zeleznik and Gordon (9) and Van Zeggeren and Storey (10). In this report we prefer to describe the main features and capabilities of current models rather than digress on the mathematical details of each since "... any method of calculation that can be made reliable is a good method when equilibrium compositions are the only concern" (9).

Chemical models can be further characterized by their application. The intended utilization of a model usually directs the developmental stages of choosing the type of model and the mathematical method. We have grouped current computerized models into "major schools" according to their point of origin and their application. Since the second generation models frequently used the same basic numerical approach as their predecessors, the classification into schools also tends to separate different mathematical formulations.

Major Schools of Computerized Models

Generalized Method of the Equilibrium Constant Approach. The basic mathematics of the equilibrium constant approach was derived in general form by Brinkley (11,12) and Kandiner and Brinkley (13). The development of the equations was well suited for adaptation to digital computers and Feldman, et al. (14) utilized the approach to calculate the equilibrium composition of high temperature gaseous mixtures. This approach has been strongly favored by geochemists. For example, Crerar (15) has revised this method so that arbitrary independent equilibrium constants can be used. He employed Newton-Raphson iteration with curve-crawler techniques (16) for rapid convergence and applied his routine to problems of hydrothermal chemistry. It should be pointed out that these methods are completely general, in the mathematical sense, so that only the reactions taking place in the system under investigation need be coded for computation. This routine can be useful for laboratory and experimental systems where most of the species and associated data base of non-general programs are unnecessary.

Generalized Method of the Gibbs Free Energy Minimization. The mathematical formulation of the free energy approach was pioneered by White et al. (17) who pointed out the advantages of using alternative numerical techniques such as steepest descent and linear programming. Dayhoff et al. (18) computed equilibrium compositions for prebiological and planetary atmospheres with this approach and showed how these compositions changed at different temperatures and pressures for systems containing C, H, O, N, P, S and Cl. Holloway and Reese (19) have solved the equilibrium composition of the system C-O-H-N at high temperatures by a computerized free energy minimization model and Karpov and Kaz'min (20) have computed the distribution of species in seawater using a dual algorithm technique. For relatively simple systems where the free energies are available and reliable, the Gibbs minimization approach is convenient and dependable. For large complex systems, however, the equilibrium constant approach is preferred. If and when an accurate and internally consistent set of thermodynamic data becomes available, the Gibbs minimization will likely find greater use. We now present a brief review of non-general computerized models which uses the equilibrium constant approach and incorporates individual reactions as part of the program.

Specific Programs in Analytical Chemistry. Following the lead of Brinkley and others, several programs were independently developed to solve problems involving aqueous equilibria in analytical and physical chemistry. One of the earliest programs, HALTAFALL, came from the work of Sillen and his

colleagues (21,22). This program was designed to calculate species distribution in an aqueous phase from a knowledge of the appropriate stability constants and total concentrations. The program is general enough to handle mixing problems such as titrations involving separation of gaseous or solid phases and organic solvent extractions. The computations are carried out at constant ionic strengh and constant temperature although these restrictions can be modified by the programmer. When apparent stability constants at different ionic strengths than the equilibrium problem are used, corrections are made by the Davies equation (80). The general method of calculation is by successive approximation. A companion program, LETAGROP VRID, was written to calculate stability constants for aqueous complexes from various measurements (23). Both programs are written in ALGOL. Perrin (24) and Perrin and Sayce (25) developed the COMICS program for the calculation of the equilibrium distribution of species using a type of "brute force" successive approximation (see below). COMICS has gone through several stages of modification which have been discussed by Leggett (1) and will not be further elaborated on here, except to mention a more recent version called SIAS (26). A similar program named EQBRAT is described by Detar (27) and it complements other programs (all in FORTRAN) which can handle a wide range of chemical problems. Bos and Meershoek (28) introduced Newton's method to titration calculations with the program EQUIL, written in PL/1, which increased the computation efficiency and was protected against non-convergence problems.

Successive Approximation Programs For Natural Water Equilibria. Garrels and Thompson (29) were the first to use the method of successive approximation in a hand calculation to solve an equilibrium problem in aqueous geochemistry. Their analysis of the species distribution in seawater in terms of ion association influenced the development of several models. Barnes and Clarke (30) found this approach useful in the investigation of the corrosion properties of wells and developed the WATCHEM program to interpret iron corrosion processes. This approach was also used to initialize PATHI (31) by a subroutine called SOLSAT which existed as a separate program. A recent version of this program, called EQUIL, has evolved from the work of Fritz (32) and Droubi (33) and it is used with the programs DISSOL and EVAPOR mentioned below. The most general first-generation programs of this type are WATEQ (34,35), SOLMNEQ (36), and EQ3 (37). All three programs have been designed to accept water analyses with on site values for pH, Eh and temperature. There is no proton mass balance condition, only mass balances on cations and anions are carried out. SOLMNEQ carries a data base in the form of a table of equilibrium constants for the range 0-350°C and EQ3 contains a similar data base for 0-300°C whereas WATEQ uses the Vant

Hoff equation or analytical expessions for equilibrium constants as a function of temperature and is considered reliable for the range 0-100°C. SOLMNEQ has additional features such as the silica and Na-K-Ca geothermometers for evaluating geothermal reservoir temperatures and includes several more trace element species than WATEQ. SOLMNEQ has been expanded to include organic complexes and ion exchange equilibria and uses the pressure dependence of the equilibrium constants. EQ3 also uses pressure dependent equilibrium constants. WATEQ was originally written in PL/1 and has been revised and translated into FORTRAN by Plummer et al. (38) in a program called WATEQF. Manganese speciation has been added to WATEQF and the successive approximation procedure was revised to give much faster convergence. 21 aqueous species and 17 minerals of uranium have been added to WATEQF in a recent modification (39). The advantages of using PL/1 optimizing code with reorganization into several subprogram blocks along with the expansion of the data base to include several trace elements and the rapid convergence of WATEQF have been incorporated into WATEQ2 (40). A shorter version, called WATSPEC, which is preferrable for handling routine water analyses has been published by Wigley (41).

The method of successive approximations has been conveniently described by Wigley (41) where either a "brute force" method or a "continued fraction" method can be used. The brute force method is the classical approach where mass action expressions are substituted directly into the mass balance conditions and solved for total concentrations which are then compared to the analytical values. In the continued fraction method, the non-linear equations are rearranged to solve for free ion concentrations which are initially assumed to be equal to the total concentrations, as detailed by Wigley (42). These two methods are best illustrated by a simple example. Assume a solution which contains free Ca^{2+} ions, free CO_3^{2-} ions, and only one ion pair: $CaCO_3^\circ$. The mass balance conditions are given by

$$mCa(total) = mCa^{2+} + mCaCO_3^\circ \quad (1)$$

$$mCO_3(total) = mCO_3^{2-} + mCaCO_3^\circ \quad (2)$$

with the restriction that (assuming an ideal solution)

$$K = \frac{mCaCO_3^\circ}{(mCa^{2+})(mCO_3^{2+})} \quad \text{or} \quad mCaCO_3^\circ = K(mCa^{2+})(mCO_3^{2-}) \quad (3)$$

Substituting equation 3 into equations 1 and 2 gives

$$mCa(total) = mCa^{2+} + K(mCa^{2+})(mCO_3^{2-}) \quad (4)$$

and $mCO_3(total) = mCO_3^{2-} + K(mCa^{2+})(mCO_3^{2-})$. (5)

Using the brute force method,

$$mCa^{2+} = mCa(total) - K(mCa^{2+})(mCO_3^{2-}) \quad (6)$$

$$mCO_3^{2-} = mCO_3(total) - K(mCa^{2+})(mCO_3^{2-}) \quad (7)$$

where mCa^{2+} and mCO_3^{2-} are assumed equal to mCa(total) and mCO_3(total) for the first estimate. Equations 6 and 7 give new values for the free ion concentrations which are then used in the next iteration. Using the continued fraction method equations 4 and 5 are rearranged to

$$mCa^{2+} = \frac{mCa(total)}{1 + KmCO_3^{2-}} \quad (8)$$

$$mCO_3^{2-} = \frac{mCO_3(total)}{1 + KmCa^{2+}} \quad . \quad (9)$$

As before, the first estimate is made by assuming that free ion concentrations are equal to total concentrations but the second estimate comes from equations 8 and 9 which vary less than equations 6 and 7 because of the form of the equation.

This alternate form of the equations produces a faster convergence as shown in an example given by Wigley (41) and also converges more rapidly than Newton-Raphson. EQ3 employs an additional control on the continued fraction method which generates monotone sequences (43,44). Its chief virtues are strict error bounds and increased stability with respect to a wide range of analyses of aqueous solutions used as input.

Other programs of this general type include SEAWAT (45) which was specifically designed for seawater calculations, MIRE (46) which was specifically designed for anoxic marine pore waters, IONPAIR and NOPAIR (47) and CALCITE (48) which were designed for freshwaters in carbonate terrains and KATKLE 1 (49) which has been used for soil water geochemistry.

Newton-Raphson Programs for Experimental and Natural Water Equilibria. Morel and Morgan (49) developed the FORTRAN program REDEQL for the calculation of multicomponent metal-ligand equilibria with considerable flexibility and includes a large number of metal-ligand complexes. The program is based on the equilibrium constant approach and uses Newton-Raphson iteration to find the solution to a function which compares the difference between the total calculated component concentration and the total analytical component concentration. REDEQL has the capability of imposing mineral saturation to allow dissolution and/or precipitation of various solids. Another option is

the calculation of interaction intensities and capacities (50,51,52). This program and its subsequent modifications have led to several "second generation" programs which are widely used by environmental engineers: REDEQL2, MINEQL and GEOCHEM. This family of programs can simulate adsorption behavior using the James-Healy approach, the Schindler-Stumm complexation approach or a combination of surface complexation and electric double layer (53-59). These programs also contain a data base for a constant temperature of 25°C, other temperatures cannot be calculated without changing all the equilibrium constants to those temperatures. MINEQL (60) has greater clarity and flexibility in a more compact program which utilizes Gaussian elimination to solve the matrix equation. GEOCHEM (61, unpublished data) has a greatly expanded data base covering over 800 organic species and more than 2000 inorganic species and it includes ion exchange reactions for simulating soil water reactions. Convergence problems are occasionally encountered with Newton-Raphson methods which are commonly caused by poor estimates of initial concentrations supplied by the programmer. However, several numerical techniques including under-relaxation, curve-crawling and pre-iteration optimization of starting estimates can greatly increase the reliability of the Newton-Raphson method (15,37,62). A good example is provided by the program EQUIL (62) which utilizes matrix scaling, eigen vector analysis, matrix modifications and a convergence forcer to achieve rapid and reliable convergence.

Reaction Path Simulation. The first application of computer techniques to problems of mass transfer in geochemistry began with the work of Helgeson and colleagues (63,64). The general approach of the program PATHI (31) is to describe a partial equilibrium reaction path (e.g. mineral dissolution and rock weathering) in terms of ordinary differential equations which are linear and can be solved by matrix algebra. The initial condition, which consists of an aqueous fluid, must be calculated by a species distribution iteration scheme such as the successive approximation method. Progressive reaction states can be computed by incrementing the progress variable, ξ (65), iteratively and checking the aqueous phase for saturation at each step and then dissolving or precipitating the required mass(es) of the appropriate mineral phase(s) to retain equilibrium. Thus, by integrating a set of differential equations a reaction path can be followed progressively until overall chemical equilibrium is reached by the specified system. This method has been applied to the study of weathering reactions, diagenesis, metamorphism and hydrothermal metasomatism (64), in the formation of ore deposits (66) and scaling of conduits caused by precipitation from geothermal brines (67). PATHI has been revised and modified to simulate granite weathering (32)and evaporation of closed basin lakes

(36) with the programs DISSOL and EVAPOR which use a related program, EQUIL, to calculate species distribution. These programs have been applied to the prediction of soil salinity and optimal irrigation doses as well as the general evolution of soil water during evaporation (68,69).

Several difficulties with PATHI led to very long execution times and occasional abnormal program termination. Claude Herrick and others (67) greatly improved the efficiency by adopting high-order Gear integration techniques (70,71). However, drift error incurred in the integration remains an annoyance, and the differential equation approach cannot be applied if the starting solution is supersaturated with any solids.

Wolery (37) has written a PATHI-like program, EQ6, which uses the Newton-Raphson method to solve the system of algebraic equations instead of their differential counterparts at each stage of reaction progress. The drift problem is thereby avoided. Taylor's series expressions, based on finite differences, are utilized to follow the course of the simulation and to predict starting estimates at each new point of reaction progress. EQ6 has some affinities in its numerical approach to the REDEQL school and Crerar's (15) program and it can precipitate an equilibrium assemblage of precipitates from an initially supersaturated solution.

Another program well suited for reaction path simulation is MIX2 (72) which uses a regression technique on the charge balance condition for the aqueous phase in computing pH after a reaction step. MIX2 can solve problems in mixing and titration of aqueous solutions (73,74), evaporation, heterogeneous equilibrium, and non-equilibrium heterogeneous reactions (75). Although MIX2 avoids the drift problems associated with PATHI, the aqueous model is limited to the major species in the system CaO-MgO-Na_2O-K_2O-H_2SO_4-H_2CO_3-HCl-H_2O and considers only one phase boundary at a time. More advanced mass transfer programs using a log linearization technique for simultaneous solution of mass action, mass balance and charge balance equation are in preparation (76) which have broad applications to mass transfer problems.

Test Case Results

Collectively, the programs mentioned above represent the "state of the art" in the calculation of the equilibrium distribution of species in aqueous systems. As a means of examining the consistency of these programs, two test cases (a dilute river water and an average seawater analysis) were compiled and mailed to more than fifty researchers who have been active in the field of chemical modeling. These test cases may overlook many of the features of specific programs, but they provide a common basis by which most of the programs can be

compared. One approach to the comparison of aqueous models is to tabulate and examine the thermodynamic data, activity coefficients, choice of complexes, etc. Alternatively the approach taken in this survey has been to examine the results predicted by the aqueous models, an approach that integrates all the aspects of each model. In this manner the differences between models can be seen in terms of the actual results which are of value in applications to specific problems. Differences will always be apparent between the thermodynamic data base used in different models but it is difficult to ascertain whether a certain difference has any effect on the final result unless the results are all compared. It should be emphasized, however, that any type of comparison will always be inadequate because any criterion that is chosen as a basis for comparison is usually not given the same priority by another model. For example, models that are developed for reaction path simulation may sacrifice computation efficiency on a species distribution calculation if more efficiency is gained in the reaction progress calculation. In this instance, as in many others, the computerized model is developed for a specific purpose and design priorities are assigned accordingly.

Each researcher was asked to complete a questionnaire describing the details of their program and to return the computed results on the two test cases. The responses received include representatives of most of the major aqueous models known. Table I identifies the programs and researchers who supplied the information for the particular program and includes general information on types of computers used, number of cards in the source deck, primary and secondary references and availability.

Table II gives a general description of the program features such as total number of elements, aqueous species, gases, organic species, redox species, solid species, pressure and temperature ranges over which calculations can be made, an indication of the types of equations used for computing activity coefficients, numerical method used for calculating distribution of species and the total number of iterations required by these models for each of the two test cases. The chemical analyses for the two test cases are summarized in Table III. The seawater compilation was prepared in several units to assure consistency between concentrations for proper entry into the aqueous models.

The results of the river water and seawater test cases computed by the aqueous models listed in Table I are summarized in Tables IV-X. Tables IV and V compare selected major and minor species computed for the river water test case, and Tables VI and VII make a similar comparison for the seawater test case. Table VIII compares activity coefficients computed for the major species in seawater and Table IX and X tabulate saturation indices for selected minerals in the river water and seawater test

cases. The saturation index, SI, is defined as log IAP/Ksp where IAP is the ion activity product for the mineral and Ksp is the thermodynamic solubility product constant.

Discussion

The remainder of this paper is a plea for caution and restraint in interpreting the results of the test cases shown here, and in the use of computerized chemical models in general. Tables IV-X show both remarkable agreement and disagreement. In general, there is better agreement between the major species concentrations than the minors and the results for the river water tend to agree better than those for seawater. We would expect better agreement in the river water test case because of the smaller amount of complexing in the more dilute solution and the more consistent and reliable activity coefficients which can be obtained at low ionic strength.

There are several limitations which lead to the discrepancies in Tables IV-X. First of all, no model will be better than the assumptions upon which it is based. The models compiled in this survey are based on the ion association approach whose general reliability rests on several non-thermodynamic assumptions. For example, the use of activity coefficients to describe the non-ideal behavior of aqueous electrolytes reflects our uncertain knowledge of ionic interactions and as a consequence we must approximate activity coefficients with semi-empirical equations. In addition, the assumption of ion association may be a naive representation of the true interactions of "ions" in aqueous solutions. If a consistent and comprehensive theory of electrolyte solutions were available along with a consistent set of thermodynamic data then our aqueous models should be in excellent agreement for most systems. Until such a theory is provided we should expect the type of results shown in Tables IV-X. No degree of computational or numerical sophistication can improve upon the basic chemical model which is utilized.

The second limitation, almost a corollary of the first, is the reliability of the equilibrium constants (or free energies) used in the model. It is quite common for solubility product constants and complex stability constants to vary by 1 to 3 orders of magnitude and have been observed to vary by that much in these models. Quite clearly this amount of uncertainty can cause large differences in the computed results and probably contributes the largest single source of error. The thermodynamic properties of substances are currently in a state of refinement by many researchers and continual updating of the aqueous models is needed. This situation is quite frustating for investigators who are involved in solute transport modeling since they need a general chemical model with a fixed data base. An internally consistent data base can be obtained

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Table I
General Information

Program Name	EQUIL	EQ3	GEOCHEM	IONPAIR	MINEQL2	MIRE	MINEQL/ REDEQL2	REDEQL2	SEAWAT	SOLMNEQ	WATEQF	WATEQ2	WATSPEC	SIAS/ COMICS
Language	FORTRAN	FORTRAN	FORTRAN	FORTRAN	FORTRAN	FORTRAN	FORTRAN	FORTRAN	FORTRAN	PL/1	FORTRAN	PL/1 (optimizing)	FORTRAN	FORTRAN
Computers	UNIVAC 1110	CDC 6400/6600 7600	IBM 360/50	IBM 370/ 165II	CDC CYBER 74	IBM 360	IBM 370	CDC CYBER 74	CDC 6400 IBM 360 IBM 370 IBM 7094 DEC 10	IBM 370	IBM 370[1]	IBM 370 Honeywell 60/68/80	ICL 1903 IBM 370	IBM 360
Number of Cards	3300	3048	3630	606	1500	420	1500	4000	184	2000	1857	3000	423	253
Primary Reference(s)	(32)	(37)	(50)	(47)	(60)	(46)	(50)	(50)	(45)	(36)	(34,35)	(34,35)	(41)	(25)
Secondary Reference(s)	(33)	(43,44)	(85)	(87,88)	(85)	(86)	(85)	(85)			(38)	(40)	(42)	(26)
Available[2] From	B. Fritz*	T.J. Wolery*	S.V. Mattigod* G. Sposito*	J. Thrail-kill*	M.R. Hoff-mann*	G.R. Holdren Jr.*	F.M.M. Morel R.E. McDuff*	M.R. Hoff-man*	G.M. Lafon*	R.L. Bassett* Y.K. Kharaka[3]	L. N. Plummer*	J.W. Ball* E.A. Jenne*	Geo Ab-stracts[4]	T. M. Florence*

[1]WATEQF is also available for use on an UNIVAC 1110 computer by contacting M.M. Reddy. [2]Coauthors who contributed data given in this and subsequent tables are identified by an asterisk,*. [3]U.S. Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025. [4]Geo Abstracts Limited, University of East Anglia, Norwich NR4 7TJ, England; price $1.70. WATSPEC calculations on subsequent tables were contributed by T.M.L. Wigley.

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Table II
Descriptive Program Features

Program Name	EQUIL	EQ3	GEOCHEM	IONPAIR	MINEQL2	MIRE	MINEQL/ REDEQL2	REDEQL2	SEAWAT	SOLMNEQ	WATEQF	WATEQ2	WATSPEC	SIAS/ COMICS
Elements[1]	20	18	44	8	38	11	*	44	7	24	19	29	16	*
Aqueous Sp.	93	140	2000	26	*	49	*	266	23	181	105	220	69	*
Gases	3	8	2	1	*	0	*	2	1	3	3	3	2	*
Organics	0	0	889	0	*	1	*	35	0	10	0	12	0	*
Redox Sp.	9	14	20	0	*	0	*	24	0	12	8	12	6	*
Minerals	120	130	185	5	*	variable	*	154	variable	158	101	309	40	*
Activity Coefficients[2]	B-dot	B-dot	Davies or B-dot	EDH	Davies	EDH	Davies	Davies	B-dot	B-dot	B-dot or Davies	B-dot or Davies	B-dot or Davies	**
Temperature Range °C	0-300	0-300	25	0-25	25	25	25	25	0-100	0-350	0-100	0-100	0-100	25
Pressure range bars	1	to steam saturation or 500 bars	1	1	1	1	1	1	1-1000	1-1000	1	1	1	1
Iteration and convergence method	explicit equations	Monotone sequences and secant method	Newton-Raphson	Free ion molalities by difference	Newton-Raphson	continued fraction	Newton-Raphson	Newton-Raphson	continued fraction	continued fraction for anions only	continued fraction	continued fraction	continued fraction	brute force
Fresh Water[3]	<10	5	-	7	†	3	†	32†	-	7	1	2	1	†
Seawater[3]	<30	6	156	-	†	5	†	57†	4	11	4	4	5	29

[1]excluding those of water. [2]EDH - extended Debye Huckel, B-dot - extended Debye Huckel with added B˙I term, Davies - Davies equation.
[3]Number of iterations where one iteration is defined as one pass through the mass action equations of the aqueous model. *depends on data base.
**Constant ionic medium. †depends on initial guess by user.

Table III
Test Case Data

River Water		Seawater*					
Species	mg/l	species	mg/kg soln	mmol/kg H_2O	mmol/l	mg/l	GFW
Na	12.	Ca	412.3	10.6617	10.5272	421.931	40.08
K	1.4	Mg	1291.8	55.08565	54.39113	1321.976	24.305
Ca	12.2	Na	10768.	485.4435	479.3230	11019.54	22.9898
Mg	7.5	K	399.1	10.5794	10.4461	408.423	39.0983
Si	8.52	Cl	19353.	565.7625	558.6293	19805.09	35.453
HCO_3^-**	75.2	SO_4	2712.	29.2615	28.8926	2775.35	96.0576
Cl	9.9	Alkal.†	141.682	2.40659	2.37625	144.992	61.0171
SO_4	7.7	Br	67.3	0.87294	0.86194	68.872	79.904
B	0.050	Sr	8.14	0.096285	0.095071	8.3302	87.62
Br	0.006	B	4.45	0.42665	0.42127	4.5540	10.81
I	0.0018	SiO_2	4.28	0.073828	0.072897	4.3800	60.0843
F	0.10	F	1.39	0.075829	0.074873	1.4225	18.9984
PO_4	0.210	Ba	0.02	0.000151	0.000149	0.0205	137.33
NO_3	0.898	I	0.062	0.0005064	0.0005000	0.06345	126.9045
NO_2	0.019	PO_4	0.06	0.000655	0.000647	0.0614	94.9714
NH_4	0.144	NO_3	0.29	0.004847	0.004786	0.2968	62.0049
Fe(II)	0.015	NO_2	0.02	0.000451	0.000445	0.0205	46.0055
Fe(III)	0.0007	NH_4	0.03	0.00172	0.00170	0.0307	18.0383
Mn	0.0044	Fe	0.002	0.0000371	0.0000366	0.00205	55.847
Al	0.005	Mn	0.0002	0.00000377	0.00000373	0.000205	54.9380
Zn	0.00049	Al	0.002	0.0000768	0.0000759	0.00205	26.9815
Cd	0.0001	Zn	0.0049	0.00007768	0.00007670	0.005014	65.38
Hg	0.00001	Cd	0.0001	0.000000922	0.000000910	0.000102	112.41
Pb	0.00003	Hg	0.00003	0.000000155	0.000000153	0.0000307	200.59
Cu	0.0005	Pb	0.00005	0.000000250	0.000000247	0.0000512	207.2
Co	0.0005	Cu	0.0007	0.0000114	0.0000112	0.000716	63.546
Ni	0.0018	Co	0.00005	0.000000879	0.000000868	0.0000512	58.9332
Cr	0.0005	Ni	0.0017	0.00002056	0.00002030	0.001740	58.71
Ag	0.00004	Cr	0.0003	0.00000598	0.00000590	0.000307	51.996
Mo	0.0005	Ag	0.00004	0.000000384	0.000000379	0.0000409	107.868
As	0.002	Sb	0.00033	0.000002809	0.000002774	0.0003377	121.75
H_2S	0.002	Mo	0.005	0.0000540	0.0000533	0.00512	95.94
DO	10.94	As	0.004	0.0000553	0.0000546	0.000409	74.9216
Eh (V)	0.440	Li	0.181	0.027027	0.026686	0.18523	6.941
DOC	2.5	Rb	0.117	0.0014188	0.0014009	0.11973	85.4678
T°C	9.5	Cs	0.0004	0.00000312	0.00000318	0.00409	132.9054
pH	8.01	DO				6.6	
Density	1.00	Eh (V)	0.500				
		T°C	25.0				
		pH	8.22				
		Density	1.02336				

*Original data are in ppm, except total titration alkalinity which is 2.322 meq/kg soln. All other units have been derived from these values using: density = g/cc, salinity = 35.0/oo, kg soln/kgH_2O = 1.03642731, and the values of Gram Formula Weight given. The derived units are given to two additional significant figures. **Titration alkalinity as HCO_3^-. † Total titration alkalinity is 2.322 meq/kg soln, expressed here as HCO_3^-. The total titration alkalinity includes carbonate as well as non-carbonate alkalinity. Instead of total alkalinity, the input may be expressed as total inorganic carbon which is 2.022 mmol/kg soln, or 123.377 ppm, 126.259 mg/l, 2.06924 mmol/l, 2.09566 mmol/kgH_2O, as HCO_3^-. Alternatively total inorganic carbon may be expressed as $H_2CO_3^*$ ($H_2CO_3^* = H_2CO_3^* + CO_2^*$) + HCO_3^-(total) + CO_3^{2-}(total). In this case, $H_2CO_3^*$ is 0.742030 ppm, 0.759364 mg/l, 0.0122429 mmol/l, 0.0123992 mmol/kgH_2O; HCO_3^-(total) is 109.469 ppm, 112.026 mg/l, 1.83598 mmol/l, 1.85942 mmol/kgH_2O; and CO_3^{2-}(total) is 12.9598 ppm, 13.2625 mg/l, 0.221228 mmol/l, 0.223831 mmol/kgH_2O.

Table IV. p(m), -Log Molality, of Selected Major Species in River Water Test Case

PROGRAM	EQUIL	EQ3	IONPAIR	MINEQL2*	MIRE	MINEQL/ REDEQL2	REDEQL2	SOLMNEQ	WATEQF	WATEQ2	WATSPEC
Ca^{2+}	3.532	3.529	3.522	3.54†	3.530	3.54†	3.539	3.527	3.525	3.525	3.525
$CaSO_4^\circ$	5.537	5.578	5.6	5.58†	5.533	5.55†	5.58	5.545	5.578	5.577	5.545
$CaHCO_3^+$	5.288	5.343	-	5.17†	5.409	5.22†	5.27	5.518	5.722	5.723	5.714
$CaCO_3^\circ$	5.681	5.933	6.	5.76†	5.732	5.82†	5.27	5.959	6.000	6.001	5.992
Mg^{2+}	3.523	3.519	3.518	3.53	3.521	3.54	3.53	3.519	3.519	3.519	3.520
$MgSO_4^\circ$	5.586	5.750	5.7	5.47	5.593	5.45	5.47	5.726	5.767	5.756	5.600
$MgHCO_3^+$	5.636	5.491	5.6	5.16	5.568	5.21	5.25	6.027	5.495	5.496	5.486
$MgCO_3^\circ$	5.470	6.133	6.	5.55	5.988	5.61	5.65	5.622	6.156	6.157	6.147
Na^+	3.283	3.282	3.283	3.28	3.284	3.28	3.28	3.283	3.283	3.283	3.283
$NaSO_4^-$	6.447	6.819	7.	6.82	7.280	6.81	6.82	6.617	6.819	6.820	6.793
$NaHCO_3^\circ$	6.505	-	-	-	6.500	-	-	6.496	6.495	6.496	6.494
K^+	4.446	4.446	4.45	4.45	4.444	4.45	4.45	4.446	4.446	4.446	4.446
KSO_4^-	7.830	7.896	-	7.59	7.819	7.58	7.60	7.942	7.935	7.936	7.910
SO_4^{2-}	4.129	4.122	4.12	4.14	4.128	4.15	4.14	4.122	4.121	4.121	4.164
Cl^-	3.401	3.554	3.554	3.55	3.556	3.55	3.55	3.558	3.554	3.554	3.554
HCO_3^-	2.924	2.920	2.915	2.93	2.919	2.91	2.93	2.918	2.917	2.917	2.917
CO_3^{2-}	5.164	5.346	5.3	5.01	5.168	5.11	5.12	5.328	5.334	5.333	5.333
$B(OH)_3^\circ$	5.361	-	-	5.37	-	-	-	5.379	5.354	5.355	5.355
$B(OH)_4^-$	6.570	-	-	6.41	-	-	6.42	6.726	6.690	6.711	6.688
Br^-	-	-	-	7.12	-	-	7.12	-	7.124	7.124	7.120
F^-	5.281	-	-	5.29	-	-	5.29	5.282	5.284	5.284	-
$H_4SiO_4^\circ$	3.528	-	-	3.53†	-	-	3.53†	3.523	3.851	3.520	3.520
H^+	7.988	7.989	-	-	-	8.01	-	7.990	7.987	7.987	7.987
OH^-	5.966	6.518	6.	5.94	5.967	-	5.95	6.525	6.502	6.501	6.502
Ionic Strength	.00238	.00239	.00240	.00300	.0024	-	.00300	.00240	.00240	.00241	.00239

*Calculated at 25°C. †MINEQL2 and REDEQL2 results were calculated in such a way that the solution was equilibrated with supersaturated phases. P, Fe, Al and Si species are not exactly comparable to the same species from the other programs because of this equilibrium process and, of course, all species have been affected to some degree.

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Table V

p(m), - Log Molality, of Selected Minor Species in River Water Test Case

PROGRAM	EQUIL	EQ3	IONPAIR	MINEQL2*	MIRE	REDEQL2	SOLMNEQ	WATEQF	WATEQ2	WATSPEC
Cr^{3+}	-	-	-	20.02	-	16.15	-	-	-	-
Mn^{2+}	7.100	8.205	-	7.14	7.138	7.13	7.099	7.119	7.119	-
$MnOH^{+}$	-	11.403	-	9.28	9.804	9.28	-	10.264	10.347	-
$MnSO_4^{\circ}$	9.166	10.383	-	9.18	9.213	9.18	9.289	9.864	9.864	-
Fe^{2+}	6.711	6.639	-	15.18†	6.896	15.18†	8.389	12.167	6.579	11.953
$FeOH^{+}$	7.075	7.428	-	15.82†	6.855	15.83†	26.711	14.257	8.669	13.860
Fe^{3+}	19.04	16.212	-	20.88†	-	20.640†	25.811	17.635	18.596	17.408
$Fe(OH)_4^{-}$	-	8.072	-	10.44†	-	10.35†	18.172	6.989	8.340	7.028
Ni^{2+}	-	-	-	7.59	-	7.93	-	-	8.892	-
$NiCO_3^{\circ}$	-	-	-	-	-	7.76	-	-	7.539	-
Cu^{2+}	10.15	8.763	-	9.67	-	10.42	14.772	-	11.293	-
$Cu(OH)_2^{\circ}$	-	-	-	13.68	-	13.22	-	-	9.045	-
Ag^{+}	-	9.660	-	-	-	15.51	9.651	-	15.891	-
$AgHS^{\circ}$	-	-	-	-	-	-	-	-	9.432	-
Zn^{2+}	8.131	8.129	-	8.15	-	8.48	7.129	-	8.504	-
$ZnCO_3^{\circ}$	-	-	-	-	-	8.51	-	-	8.720	-
$Zn(HS)_2^{\circ}$	-	-	-	-	-	-	-	-	8.790	-
Cd^{2+}	-	-	-	9.10	-	9.41	-	-	11.612	-
$CdOH^{+}$	-	-	-	10.15	-	11.46	-	-	12.651	-

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$CdHS^+$	-	-	-	-	-	-	-	-	9.078	-
Hg^{2+}	-	16.875	-	21.07	-	20.15	41.872	-	-	-
Al^{3+}	15.69	13.697	-	17.49†	-	17.164†	13.598	13.908	15.565	14.778
$Al(OH)_4^-$	7.090	6.732	-	8.66	-	8.37†	6.765	6.741	8.406	6.733
Pb^{2+}	9.845	14.380	-	12.07	-	11.93	9.843	-	11.749	-
$PbOH^+$	-	-	-	11.21	-	11.68	-	-	10.378	-
$PbCO_3^\circ$	-	9.839	-	9.89	-	9.86	-	-	10.025	-
NO_3^-	4.839	-	4.84	-	-	-	4.839	4.839	4.839	4.839
NH^+	5.098	-	-	5.14	-	5.13	5.105	5.106	5.106	10.392
PO_4^{3-}	10.03	-	-	11.41†	-	11.40†	10.189	10.156	10.156	-
HPO_4^{2-}	5.818	-	-	7.07†	5.773	7.16†	5.813	5.793	5.793	-
$H_2PO_4^-$	6.694	-	-	7.78†	6.654	8.06†	6.622	6.625	6.625	-
$HAsO_4^{2-}$	-	-	-	-	-	-	13.990	-	7.595	-
$H_2AsO_4^-$	-	-	-	-	-	-	15.046	-	8.885	-
S^{2-}	-	17.140	-	-	-	-	16.489	12.613	12.870	12.615
HS^-	-	7.268	-	-	-	-	7.299	7.288	7.544	7.288
H_2S°	-	8.076	-	-	-	-	8.071	8.146	8.403	8.146
I^-	-	-	-	7.785	-	7.86	-	-	-	-

*Calculated at 25°C. †MINEQL2 and REDEQL2 results were calculated in such a way that the solution was equilibrated with supersaturated phases. P, Ca, Fe, Al and Si species are not exactly comparable to the same species from the other programs because of this equilibration process, and, of course, all species have been affected to some degree.

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Table VI

p(m), -Log Molality, of Selected Major Species in Sea Water Test Case

PROGRAM	EQUIL	EQ3	GEOCHEM	K+K*	MINEQL2	MIRE	MINEQL/ REDEQL2	REDEQL2	SEAWAT	SIAS	SOLMNEQ	WATEQF	WATEQ2	WATSPEC
Ca^{2+}	2.013	2.027	2.21	2.024	2.12†	2.074	2.03	2.11†	2.053	2.058	2.013	2.024	2.025	2.023
$CaSO_4^\circ$	3.062	2.928	3.12	3.046	3.00†	2.744	2.97	3.00†	2.764	2.781	3.056	2.940	2.938	2.947
$CaHCO_3^+$	4.261	4.234	4.48	4.504	4.92†	4.366	4.26	4.84†	4.242	4.285	4.261	4.481	4.449	4.465
$CaCO_3^\circ$	4.636	4.540	4.59	4.755	5.30†	4.734	4.63	5.30†	4.715	4.365	4.635	4.649	4.616	4.665
$CaCl^+$	-	-	2.46	-	-	-	-	-	-	-	-	-	-	-
Mg^{2+}	1.304	1.319	1.46	1.328	1.34	1.322	1.33	1.34	1.347	1.357	1.299	1.311	1.312	1.310
$MgSO_4^\circ$	2.305	2.175	2.47	2.190	2.11	2.299	2.17	2.13	2.008	2.080	2.360	2.235	2.222	2.241
$MgHCO_3^+$	3.777	3.554	3.83	3.405	4.14	3.676	3.60	4.06	3.588	2.684	3.834	2.655	3.624	3.597
$MgCO_3^\circ$	3.619	3.940	4.14	3.745	4.32	3.684	3.67	4.32	4.121	4.664	3.689	4.045	4.014	4.062
$MgCl^+$	-	-	1.79	-	-	-	-	-	-	-	-	-	-	-
Na^+	0.336	0.320	0.41	0.328	0.34	0.335	0.33	0.34	0.321	0.314	0.336	0.320	0.320	0.323
$NaSO_4^-$	1.964	2.208	1.94	2.286	2.18	2.716	2.20	2.19	2.107	-	1.965	2.178	2.195	2.146
$NaHCO_3^\circ$	3.873	-	3.40	3.466	-	3.851	3.84	-	-	-	3.860	3.785	3.752	3.807
K^+	1.982	1.983	2.04	2.007	2.01	2.000	1.99	2.01	1.981	1.976	1.982	1.983	1.983	1.985
KSO_4^-	3.839	3.748	3.76	3.802	3.45	3.789	3.67	3.46	3.916	-	3.871	3.768	3.766	3.736
Cl^-	0.257	0.247	0.33	0.25	0.25	0.265	0.25	0.25	0.247	0.253	0.256	0.247	0.247	0.249
SO_4^{2-}	1.906	1.823	2.11	1.804	1.91†	1.836	1.84	1.89†	2.009	1.723	1.881	1.811	1.808	1.822
HCO_3^-	2.884	2.816	2.87	2.792	3.56	2.815	2.90	3.39	2.808	-	2.885	2.825	2.836	2.845
CO_3^{2-}	4.419	4.371	4.48	4.622	4.91	4.415	4.46	4.89	4.369	5.507	4.484	4.422	4.566	4.443
$B(OH)_3^\circ$	3.435	-	3.51	-	3.49	-	3.45	3.48	-	-	3.506	3.430	3.431	3.481
$B(OH)_4^-$	4.226	-	4.23	-	4.06	-	4.20	4.10	-	-	4.234	4.257	4.255	4.015
Br^-	-	-	3.06	-	3.07	-	-	3.07	3.059	3.065	-	3.059	3.059	3.059

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F^-	4.228	-	4.36	-	4.39	-	-	4.38	-	4.411	4.379	4.410	4.410	-
MgF^+	4.792	-	4.53	-	4.56	-	-	4.58	-	-	4.464	4.442	4.443	-
Sr^{2+}	4.016	-	4.28	-	4.13†	-	-	4.119†	-	-	4.045	4.016	4.016	4.016
$H_4SiO_4^\circ$	4.155	4.159	4.16	-	4.19†	-	-	4.17†	-	-	4.161	4.145	4.145	4.147
H^+	8.125	8.126	8.15	7.966	-	-	-	-	8.095	-	8.125	8.093	8.093	8.098
OH^-	5.603	5.606	5.65	6.038	5.46	5.552	-	5.54	5.613	-	5.601	5.660	5.660	5.571
Ionic Strengh	0.663	0.6772	0.5298	-	0.65	0.655	-	0.65	0.6595	-	0.6662	0.6801	0.6799	0.6770

*Karpov and Kaz'min (1972) using Gibbs free energy minimization on a similar seawater. †MINEQL2 and REDEQL2 results were calculated in such a way that the solution was equilibrated with supersaturated phases. Si, Al, Fe, Ca, Sr, Ba, Zn SO_4, and PO_4 species are not exactly comparable to the same species from the other programs because of this process, and, of course, all species have been affected to some degree.

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Table VII

p(m), -Log Molality, of Selected Minor Species in Seawater Test Case

PROGRAM	EQUIL	EQ3	GEOCHEM	MINEQL2	MIRE	REDEQL2	SIAS	SOLMNEQ	WATEQF	WATEQ2	WATSPEC
Li^+	4.572	-	4.66	-	-	-	-	4.568	4.573	4.573	4.573
Rb^+	-	-	5.87	-	-	-	-	-	-	5.848	-
Cs^+	-	-	8.56	-	-	-	-	-	-	8.506	-
Ba^{2+}	-	-	6.93	8.03†	-	8.01†	-	6.857	6.821	6.821	6.821
Cr^{3+}	-	-	25.63	28.34	-	24.55	-	-	-	-	-
Mn^{2+}	8.456	9.287	9.33	8.96	8.592	8.94	-	8.478	8.654	8.654	-
$MnCl^+$	-	-	10.26	8.74	9.067	8.75	-	29.376	8.880	8.881	-
Fe^{3+}	18.740	17.466	22.94	20.71†	-	20.26†	-	-	17.897	17.897	17.714
$Fe(OH)_3^\circ$	-	-	11.28	17.10†	-	24.14†	-	-	8.071	8.071	7.805
$Fe(OH)_4^-$	-	7.439	12.41	9.96†	-	9.94†	-	-	7.664	7.664	7.678
Ni^{2+}	-	-	9.23	7.77	-	7.92	7.834	-	-	8.813	-
$NiCl_2^\circ$	-	-	9.74	-	-	8.10	-	-	-	9.335	-
$NiCO_3^\circ$	-	-	7.91	5.75	-	8.61	-	-	-	7.590	-
Cu^{2+}	13.152	9.056	11.21	11.35	-	11.32	9.579	-	-	10.153	-
$Cu(OH)_3^\circ$	-	-	12.40	3.22	-	9.06	-	-	-	7.985	-
$CuCO_3^\circ$	-	-	10.01	10.82	-	10.80	-	-	-	9.070	-
Ag^+	-	14.797	16.79	16.82	-	16.79	-	14.477	-	14.394	-
$AgCl_4^{3-}$	-	9.517	12.48	12.08	-	12.05	-	9.617	-	9.684	-
Zn^{2+}	7.323	7.346	8.35	7.74†	-	8.06†	7.690	7.321	-	7.547	-
$ZnCO_3^\circ$	-	-	7.33	-	-	8.95†	-	-	-	7.894	-
Cd^{2+}	-	-	11.11	10.59	-	10.70	10.606	-	-	11.257	-
$CdCl^+$	-	-	9.99	9.47	-	9.41	-	-	-	9.371	-

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$CdCl_2^\circ$	-	-	9.94	9.34	-	9.48	-	-	-	9.369	-
Hg^{2+}	-	23.310	-	-	-	-	-	23.426	-	-	-
$HgCL_3^-$	-	9.816	-	-	-	-	-	9.965	-	-	-
Al^{3+}	15.963	16.076	16.37	16.67†		16.15†		19.277	15.956	16.091	16.996
$Al(OH)_3^\circ$	7.600	-	7.72	-	-	7.58†	-	-	-	7.665	-
$Al(OH)_4^-$	7.287	7.114	7.25	7.53†	-	7.32†	-	10.611	7.115	7.259	7.114
Pb^{2+}	10.446	13.746	11.68	-	-	-	-	10.442	-	11.335	-
$PbCl_2^\circ$	10.380	13.591	11.41	-	-	-	-	0.372	-	11.017	-
$PbCO_3^\circ$	-	9.602	10.09	-	-	-	-	9.743	-	9.743	-
NO_3^-	5.315	-	5.30	-	-	-	-	-	5.315	5.314	5.315
PO_4^{3-}	9.979	-	10.48	11.81†	-	11.76†	-	10.126	10.482	10.480	-
HPO_4^{2-}	6.858	-	7.02	8.48†	6.673	8.48†	-	6.897	6.989	6.988	-
$H_2PO_4^-$	8.474	-	8.49	9.93†	8.295	10.06†	-	8.449	8.382	8.381	-
AsO_4^{3-}	-	-	11.01	-	-	-	-	-	-	10.007	-
$HAsO_4^{3-}$	-	-	8.45	-	-	-	-	-	-	7.264	-
I^-	-	-	6.30	6.30	-	6.31	-	-	-	6.296	-

†MINEQL2 and REDEQL2 results were calcualted in such a way that the solution was equilibrated with supersaturated phases. Si, Al, Fe, Ca, Sr, Ba, Zn, SO_4, and PO_4 species are not exactly comparable to the same species from the other programs because of this process, and of course, all species have been affected to some degree.

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Table VIII
Activity Coefficients of Selected Major Species in Sea Water

PROGRAM	EQUIL	EQ3	MIRE	SEAWAT	SOLMNEQ	WATEQF	WATEQ2
Ca^{2+}	0.245	0.245	0.231	0.245	0.244	0.249	0.249
$CaSO_4^\circ$	1.172	1.000	0.507	1.150	1.180	1.170	1.170
$CaHCO_3^+$	0.714	0.714	0.589	0.669	0.737	0.747	0.747
$CaCO_3^\circ$	1.172	1.000	1.123	1.150	1.180	1.170	1.170
Mg^{2+}	0.315	0.315	0.296	0.314	0.263	0.288	0.288
$MgSO_4^\circ$	1.172	1.000	1.123	1.150	1.180	1.170	1.170
$MgHCO_3^+$	0.671	0.670	0.589	0.669	0.670	0.747	0.747
$MgCO_3^\circ$	1.172	1.000	0.387	1.150	1.180	1.170	1.170
Na^+	0.671	0.670	0.631	0.688	0.670	0.706	0.706
$NaSO_4^-$	0.683	0.682	0.589	0.669	0.720	0.747	0.747
$NaHCO_3^\circ$	1.172	-	1.123	1.150	1.180	1.170	1.170
K^+	0.626	0.626	0.589	0.625	0.626	0.622	0.622
KSO_4^-	0.650	0.647	0.589	0.669	0.720	0.747	0.747
Cl^-	0.627	0.626	0.589	0.625	0.626	0.622	0.622
SO_4^{2-}	0.618	0.167	0.158	0.167	0.167	0.181	0.181
HCO_3^-	0.690	0.690	0.631	0.669	0.720	0.675	0.747
CO_3^{2-}	0.188	0.187	0.195	0.190	0.222	0.207	0.311
$B(OH)_3^\circ$	1.172	-	-	-	1.180	1.170	1.170
$B(OH)_4^-$	0.671	-	-	-	0.605	0.747	0.747
Br^-	-	-	-	0.625	-	0.747	0.747
F^-	0.650	-	-	-	0.649	0.747	0.747
MgF^+	-	-	-	-	0.689	0.747	0.747
Sr^{2+}	0.207	-	-	-	0.207	0.311	0.311
$H_4SiO_4^\circ$	1.000	-	1.123	-	1.180	1.170	1.170
H^+	0.804	0.805	-	0.750	0.804	0.747	0.747
OH^-	0.650	0.649	0.589	0.685	0.649	0.747	0.747
Ionic Strength	0.663	0.677	0.655	0.660	0.666	0.680	0.680

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Table IX

Saturation Index for Selected Minerals in River Water Test Case

MINERAL	FORMULA	EQUIL	EQ3	IONPAIR	MIRE	SOLMNEQ	WATEQF	WATEQ2	WATSPEC
Calcite	$CaCO_3$	-0.51	-0.585	-0.673	-0.461	-0.765	-0.634	-0.634	-0.63
Dolomite	$CaMg(CO_3)_2$	-0.73	-0.248	-1.340	-0.730	-1.329	-1.384	-1.386	-1.38
Siderite	$FeCO_3$	-1.37	+0.456	-	-2.329	-3.377	-7.347	-1.760	-7.13
Rhodochrosite	$MnCO_3$	-1.81	-3.225	-	-2.097	-2.136	-2.180	-2.180	-
Gypsum	$CaSO_4 \cdot 2H_2O$	-3.00	-2.962	-	-3.081	-2.942	-3.057	-2.969	-3.25
Celestite	$SrSO_4$	-	-	-	-	-	-	-	-
Hydroxyapatite	$Ca_5(PO_4)_3OH$	+2.82	-	-	+5.891	+5.046	-1.784	-1.722	-
Fluorite	CaF_2	-4.39	-	-	-	-3.338	-3.079	-3.074	-
Ferric Hydrox.(Am)	$Fe(OH)_3$	-	-	-	-	-7.584	+1.304	-	-
Goethite	$FeO(OH)$	+5.59	-	-	-	-1.484	+7.810	+6.843	+5.06
Hematite	Fe_2O_3	+8.11	+18.332	-	-	-3.252	+15.144	+13.223	+13.52
Gibbsite (crypt.)	$Al(OH)_3$	-0.08	+1.948	-	-	-0.058	-0.336	-1.989	-1.19
Birnessite	MnO_2	-	-	-	-	-	-4.114	-4.114	-
Chalcedony	SiO_2	-	+0.490	-	-	+0.217	-0.142	+0.189	-
Quartz	SiO_2	+0.47	+0.776	-	-	+0.697	+0.405	+0.736	+0.74
Kaolinite	$Al_2Si_2O_5(OH)_4$	+1.83	+5.826	-	-	-	+1.638	-1.021	+2.32
Sepiolite	$Mg_2SiO_{7.5}(OH) \cdot 3H_2O$	-4.55	-	-	-	-5.734	-3.699	-	-
FeS Amorphous	FeS	-	-	-	-	-	-7.644	-2.313	-
Mackinawite	FeS	-	-	-	-	-	-6.928	-1.580	-

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Table X

Saturation Index for Selected Minerals in Seawater Test Case

MINERAL	FORMULA	EQUIL	EQ3	GEOCHEM	MIRE	SEAWAT	SOLMNEQ	WATEQF	WATEQ2	WATSPEC	ACM[1]	RWR[2]
Calcite	$CaCO_3$	+0.60	+0.806	+0.67	+0.621	+0.631	+0.597	+0.742	+0.774	+0.72	+0.568 to +0.674	-
Dolomite	$CaMg(CO_3)_2$	+2.30	+3.439	+1.79	+2.277	+2.305	+2.219	+2.330	+2.394	+2.30	-	-
Siderite	$FeCO_3$	-2.65	-10.276	-12.42	-	-	-6.691	-9.006	-8.973	-8.83	-	-
Rhodochrosite	$MnCO_3$	-3.57	-4.444	-4.45	-4.077	-	-3.709	-3.727	-3.695	-	-	-
Gypsum	$CaSO_4 \cdot 2H_2O$	-0.47	-0.399	-0.76	-0.487	-0.840	-0.441	-0.439	-0.348	-0.60	-	-0.582
Celestite	$SrSO_4$	-	-	-0.13	-	-	-0.988	-0.610	-0.609	-1.32	-	-
Barite	$BaSO_4$	-	-	+1.12	-	-	-0.501	+0.097	+0.097	-0.34	-	-
Hydroxyapatite	$Ca_5(PO_4)_3OH$	+4.16	-	+3.53	+7.642	-	+7.140	+0.605	+0.670	-	-	-
Fluorite	CaF_2	-1.61	-	-2.61	-	-	-1.048	-0.742	-0.751	-	-	-
Ferric Hydr.(Am)	$Fe(OH)_3$	-	-	-2.93	-	-	-	+0.712	+0.706	-	-	-
Goethite	$FeO(OH)$	+5.64	-	+2.58	-	-	-	+7.809	+7.803	+5.04	-	-
Hematite	Fe_2O_3	+8.21	+16.518	+5.65	-	-	-	+15.228	+15.229	+13.54	-	-
Gibbsite Crypt.	$Al(OH)_3$	-0.63	+0.216	-0.57	-	-	-4.954	-1.685	-1.817	-2.69	-	-
Birnessite	MnO_2	-	-	-1.01	-	-	-	-2.993	-2.993	-	-	-
Manganite	$MnO(OH)$	-	-	-2.03	-	-	-	-1.335	-1.336	-	-	-
Chalcedony	SiO_2	-	-0.415	-1.41	-	-	-0.522	-0.537	-0.537	-0.54	-	-
Quartz	SiO_2	-0.14	-0.143	-0.04	-	-	-0.092	-0.055	-0.054	-0.06	-	-
Kaolinite	$Al_2Si_2O_5(OH)_4$	-0.47	+0.645	-0.67	-	-	-2.108	-2.108	-2.384	-2.24	-	-
Sepiolite Cryst.	$Mg_2Si_3O_{7.5}(OH) \cdot 3H_2O$	-1.96	-	+1.09	-	-	-1.908	+1.059	+1.034	-	-	-

[1]Apparent constant method (see text for explanation). [2]Calculated from the equations of Reilly, Wood and Robinson (6) by M. Lafon.

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through the approach offered by Haas and Fisher (77) but it will take some time to compile and evaluate the appropriate data. In the meantime the lack of carefully evaluated thermodynamic data will continue to be the most serious limitation for any type of chemical modeling.

Thirdly, another corollary of the first limitation, is the inconsistency and inadequacy of activity coefficient equations. Some models use the extended Delbye-Huckel equation (EDH), others the extended Debye-Huckel with an additional linear term (B-dot, 78, 79) and others the Davies equation (some with the constant 0.2 and some with 0.3, 80). The activity coefficients given in Table VIII for seawater show fair agreement because seawater ionic strength is not far from the range of applicability of the equations. However, the accumulation of errors from the consideration of several ions and complexes could lead to serious discrepancies. Another related problem is the calculation of activity coefficients for neutral complexes. Very little reliable information is available on the activity of neutral ion pairs and since these often comprise the dominant species in aqueous systems their activity coefficients can be an important source of uncertainty.

The fourth limitation is the assumption made about the redox state of aqueous systems. The distribution of redox species depends on what redox potential is assumed to dominate the chemical equilibrium. The possible alternatives include the Fe^{2+}/Fe^{3+} couple, the S^{2-}/SO_4^{2-} couple, the O_2/H_2O couple, the O_2/H_2O_2 couple, the NO_3^-/NH_4^+ couple and the redox potential measured with a platinum electrode. The wide range of values for iron, manganese, chromium and arsenic species is partly due to the inherent redox assumptions. To examine how different redox controls affect the distribution of species while other factors are kept constant, several redox options were computed on WATEQ2 for both test cases. These results are shown in Table XI. The redox elements, iron and arsenic, can be distributed according to several imposed redox potentials given total concentrations of iron and arsenic. Ferrous and ferric ions along with the two dominant forms of oxidized and reduced arsenic were computed by all the possible redox options. The range of concentrations of these species is several orders of magnitude and includes most of the values listed in Tables V and VII. If the application of a chemical model is to interpret natural water chemistry, including redox reactions, then individual redox elements such as total ferrous and total ferric should be analyzed separately when possible rather than assuming that they can be distributed according to some other equilibrium. Homogeneous redox equilibrium may not be often obtained in real systems (81) and imposed redox equilibria may not represent a realistic distribution of species.

A fifth factor is the total number of complexes considered by an aqueous model. If one model has 2 or 3 times as

Table XI
Variations in the distribution of selected redox species (in p(m)) caused by changing the imposed redox potential.

Imposed Redox Potential	Implied Eh(volts)	Fe^{2+}	Fe^{3+}	$H_2AsO_3^-$	$HAsO_4^{2-}$
River Water Test Case					
Pt Eh	0.440	11.78	17.25	25.80	7.60
O_2/H_2O	0.783	17.89	17.25	38.03	7.60
O_2/H_2O_2	0.141	6.81	17.61	15.14	7.60
NO_3^-/NO_2^-	0.445	11.87	17.25	25.98	7.60
NO_3^-/NH_4^+	0.328	9.78	17.25	21.81	7.60
S^{2-}/SO_4^{2-}	-0.532	6.56	29.36	7.59	24.04
Fe^{2+}/Fe^{3+}	0.073	6.58	18.50	12.72	7.60
Seawater Test Case					
Pt Eh	0.550	13.94	17.90	29.17	7.26
O_2/H_2O	0.731	17.85	17.90	36.98	7.26
O_2/H_2O_2	0.133	7.94	18.09	16.76	7.26
NO_3^-/NO_2^-	0.390	12.08	17.90	25.45	7.26
NO_3^-/NH_4^+	0.269	10.04	17.90	21.36	7.26

many metal-ligand complexes as another model then it will have a lower concentration of free ligand, assuming negligible differences in the data base. For example, the inclusion of the calcium and magnesium chloride complexes by GEOCHEM tends to lower the free calcium, magnesium and chloride ion concentrations below those of the other models.

A sixth source of difference, which was unavoidable in preparation of the test cases, is the various ways each program handles the carbonate system. From a practical standpoint, the inorganic carbon system of natural waters is usually determined from the titration alkalinity. Because the titration alkalinity includes both carbonate and non-carbonate alkalinity, the titration alkalinity must be corrected for non-carbonate alkalinity. Most models correct for the presence of $H_2BO_3^-$ and $H_3SiO_4^-$ but many other minor species should be considered and there is no general agreement as to the precise correction for non-carbonate alkalinity. In devising the correction used originally in WATEQ, Truesdell and Jones also

considered the possibility that some non-carbonate alkalinity species were kinetically slow to react in the titration and thus were not included in the titration alkalinity. Even if we could agree on which species to subtract from the titration alkalinity, the computed carbonate system is still dependent on the equilibrium constants and activity coefficients used by the model to compute the actual concentrations of non-carbonate alkalinity species.

Some aqueous models accept only total inorganic carbon rather than titration alkalinity or carbonate alkalinity. For this reason, the sea water analysis of Table III includes total inorganic carbon which was calculated from pH, total alkalinity and salinity using the apparent sea water constants of Mehrbach et al.(82) for the dissociation of carbonic acid and the boric acid dissociation constant of Lyman (83), as expressed by Li et al. (84).

Certainly, there are differences in aqueous models in current use and the carbonate calculations will depend in part on whether the source of carbon data was total alkalinity or total inorganic carbon from Table III. For example, using the program WATEQF and data in ppm from Table III, Table XII compares some computed parameters of the carbonate system of seawater using total alkalinity and total inorganic carbon from Table III.

Table XII

Comparison of carbonate parameters computed by WATEQF in Seawater Test Case

Computed Parameter	Inorganic Carbon Data Source: Total Alkalinity (= 141.682 ppm as HCO_3^-)	Total Inorganic Carbon (= 2.09566 x 10^{-3} m)
Total carbon (m)	2.1421 x 10^{-3}	2.0957 x 10^{-3}
$mHCO_3^-$	1.4961 x 10^{-3}	1.4636 x 10^{-3}
mCO_3^{2-}	3.7880 x 10^{-5}	3.7057 x 10^{-5}
$\log P_{CO_2}$	-3.399	-3.409
SI calcite	0.7418	0.7323

The differences shown in Table XII are really quite small and well within the uncertainties of the thermodynamic data of the aqueous model. The close agreement shown in Table XII indicates that the carbonate system of WATEQF is reasonably compatible with the apparent constants of Mehrbach et al. (82) and Lyman (83). However, in comparing results in the carbonate system computed by other aqueous models, there is a

potential for differences depending on the compatibility of the equilibrium constants and activity coefficients used with the apparent constant approach for seawater.

A seventh limitation is the fact that not all of the aqueous models compute temperature corrections. The programs of the REDEQL school and those used in analytical chemistry contain a data base of equilibrium constants at 25°C and are not as reliable at other temperatures. Since the river water test case was given a temperature of 9.5°C there will be some differences between programs that correct for temperature and those that do not. The temperature correction can cause substantial changes in computed results when interpreting the chemistry of natural waters because these systems commonly vary both diurnally and seasonally over a large range in temperature and because many equilibrium constants are strongly temperature dependent.

If all of these limitations were overcome, the aqueous models described here should give consistent results. To reemphasize, the largest single source of discrepancy is the thermodynamic data base used by each model. This limitation is not apparent among the major species in a dilute solution but as the ionic strenth increases and/or the concentration of the constituent decreases, the discrepancies markedly increase. This problem becomes particularly acute for trace elements where apparently small changes in equilibrium constants or pH or redox potential or temperature may produce very large changes in trace element speciation.

The effect of the thermodynamic data is particularly striking from a comparison of saturation indices in Tables IX and X. The mineral showing the best agreement in both test cases is calcite which would be expected since its properties have been extensively studied, especially in the marine environment. Using the apparent constant method the SI of calcite in seawater varies from 0.568 to 0.674 depending on the choice of data. The low value is that of Berner (90) which is compatible with the apparent dissociation constants for carbonic acid in seawater of Lyman (83). The high value is from Ingle et al. (88) which is compatible with the dissociation constants of Mehrbach et al. (82). In the river water test case gypsum SI values show very good agreement but for many other minerals there is considerable disagreement of one order of magnitude or more. SI values for several minerals show both supersaturation and undersaturation and these conditions are particularly striking for hydroxyapatite, goethite, hematite and kaolinite. In the seawater test case gypsum does not show as good agreement as in river water with values ranging from -0.35 to -0.84. Many minerals again show more than an order of magnitude difference in SI values. From an examination of these tables it should be clear that any interpretation of mineral saturation states in an aquatic environment depends

greatly on the chosen chemical model which, in turn, depends upon the reliability of the thermodynamic data base and any inherent assumptions of the behavior of electrolyte solutions.

Summary

In this review over 30 computerized chemical models have been described which can calculate the distribution of species in an aqueous system at equilibrium. Every computerized model was developed for somewhat different purposes and there is no general purpose model which can be used for all of the applications described in this report. However, an attempt has been made to point out the major differences between models as a guide to researchers interested in chemical modeling. The applications include titration simulation, solubility testing, adsorption modeling, ion exchange modeling, and progressive mass transfer reactions in heterogeneous systems. Two hypothetical test cases: a dilute river water analysis and a seawater analysis were run on a total of 13 different programs to determine the distribution of species and the saturation indices for several minerals. A comparison of these results demonstrate generally good agreement for the major species and rather poor agreement for the minor species. The major source of discrepancy is the thermodynamic data base used by the various models. Other important limitations include the number of complexes in each model, the form of the activity coefficient equation, the redox assumptions, the form of the alkalinity input and the non-carbonate alkalinity correction, and temperature and pressure corrections. The discrepancies in the test case results indicate that a great deal of caution must be exercised when interpreting aqueous chemical equilibria by a chemical modeling approach. More attention should be paid to the assumptions of a model and a great deal more work is needed on the evaluation of thermodynamic data in order to provide a consistent set of values.

Abstract

A survey of computer programs which are currently being used to calculate the distribution of species in aqueous solutions, especially natural waters, has been made in order to 1) provide an inventory of available programs with a short description of their uses, 2) compare the consistency of their output for two given test solutions and 3) identify major weaknesses or problems encountered from their use. More than a dozen active programs which can be used for distribution of species and activity calculations for homogeneos equilibria among the major anions and cations of natural waters have been inventoried. Half of these programs can also accept several trace elements including Fe, Al, Mn, Cu, Ni, Zn, Cd, Pb, Ag, Hg, As,

Ba, Sr, and B. Consistency between programs was evaluated by comparing the log of the molal concentrations of free ions and complexes for two test solutions: a hypothetical seawater analysis and a hypothetical river water analysis. Comparison of the free major ion concentrations in the river water test case shows excellent agreement for the major species. In the seawater test case there is less agreement and for both test cases the minor species commonly show orders of magnitude differences in concentrations. These differences primarily reflect differences in the thermodynamic data base of each chemical model although other factors such as activity coefficient calculations, redox assumptions, temperature corrections, alkalinity corrections and the number of complexes used all have an affect on the output.

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